

Description

GELLED ACID

BACKGROUND OF INVENTION

[0001] The invention relates to stimulation of production in hydrocarbon wells. More specifically it relates to gelled acids for diversion and leakoff control in matrix acidizing and acid fracturing. Most specifically it relates to reducing agents and reducing agent precursors that are less toxic to aquatic species and that leave less residue than prior reducing agents upon destruction of the crosslinking agent after treatment.

[0002] Acids are often used to treat subterranean formations to stimulate the formations to increase the production of fluids, such as hydrocarbons. When the acid is injected above the fracture pressure of the formation being treated, the treatment is called acid fracturing or fracture acidizing. The object is to create a large fracture that serves as an improved flowpath through the rock formation. After such fractures are created, when pumping of the fracture fluid is stopped and the injection pressure

drops, the fracture tends to close upon itself and little or no new flow path is left open after the treatment. Commonly, a proppant is added to the fracturing fluid so that, when the fracture closes, proppant remains in the fracture, holds the fracture faces apart, and leaves a flowpath conductive to fluids. Alternatively, instead of propping, if the formation rock is acid soluble, for example is a carbonate, an acid may be used as a component of the fracturing fluid. The acid differentially etches the faces of the fracture, creating or exaggerating asperities, so that, when the fracture closes, the opposing faces no longer match up. Consequently they leave an open pathway for fluid flow. A problem with this technique is that as the acid is injected it tends to react with the most reactive rock and/or the rock with which it first comes into contact. Thus, much of the acid is used up near the wellbore and is not available for etching of the fracture faces farther from the wellbore. Furthermore, the acidic fluid follows the paths of least resistance, which are for example either natural fractures in the rock or areas of more permeable or more acid-soluble rock. This process creates typically long branched passageways in the fracture faces leading away from the fracture, usually near the wellbore.

These highly conductive microchannels are called "wormholes" and are very deleterious because subsequently-injected fracturing fluid tends to leak off into the wormholes rather than lengthening the desired fracture. To block the wormholes, techniques called "leakoff control" techniques have been developed. This blockage should be temporary, because the wormholes are preferably open to flow after the fracturing treatment; fluid production through the wormholes adds to total production.

[0003] When an acidic fluid is used to stimulate a substantially acid-soluble producing, or potentially-producing, formation below the fracturing pressure, the treatment is called matrix stimulation or matrix acidizing. Numerous studies have shown that the dissolution pattern created by the flowing acid occurs by one of three mechanisms (a) compact dissolution, in which most of the acid is spent near the wellbore rock face; (b) wormholing, in which the dissolution advances more rapidly at the tips of a small number of wormholes than at the wellbore walls; and (c) uniform dissolution, in which many pores are enlarged. Compact dissolution occurs when acid spends on the face of the formation. In this case, the live acid penetration is commonly limited to within a few centimeters of the well-

bore. Uniform dissolution occurs when the acid reacts under the laws of fluid flow through porous media. In this case, the live acid penetration will be, at most, equal to the volumetric penetration of the injected acid. (Uniform dissolution is also the preferred primary mechanism of conductive channel etching of the fracture faces in acid fracturing, as discussed above.) The objectives of the acidizing process are met most efficiently when near well-bore permeability is enhanced to the greatest depth with the smallest volume of acid. This occurs in regime (b) above, when a wormholing pattern develops.

[0004] However, just as wormholing prevents the growth of large fractures, wormholing prevents the treatment of long horizontal or vertical regions of a formation. Once wormholes have formed, at or near a point in the soluble formation where the acid first contacts the formation, subsequently-injected acid will tend to extend the existing wormholes rather than create new wormholes further along the formation. Temporary blockage of the first wormholes is needed so that new wormholes can be formed and the entire section of the formation treated. This is called "diversion", as the treatment diverts later-injected acid away from the pathway followed by earlier-injected acid. In this

case, the blockage must be temporary because all the wormholes are needed to serve as the primary production pathway.

[0005] Commonly, the same methods may be used for "leakoff control" in acid fracturing and for "diversion" in matrix acidizing. One method is to incorporate into the acidic fluid first a chemical or chemicals that will form a barrier to fluid flow after a substantial amount of the acid is consumed ("spent") and the pH increases, and second another chemical or chemicals that will destroy the barrier as more acid is spent and the pH increases further. Such an acidic system may be termed a "leakoff control acid system" or "LCA system" or a "self-diverting acid system" or "SDA system" depending upon its use. An example of such a system is described in European Patent Application Publication No. 0 278 540 B1, assigned to the assignee of the present application. That initially strongly acidic system initially has low viscosity but includes a soluble ferric ion source and a polymeric gelling agent that is crosslinked by ferric ions at a pH of about 2 or greater but not at lower pH's. However, the polymer is not crosslinked by ferrous ions. Therefore, the system includes a reducing agent that reduces ferric ions to ferrous ions, but only at a

pH above about 3 to 3.5. Consequently, as the acid spends, for example in a wormhole, and the pH increases to about 2 or greater, the polymer crosslinks, and a very viscous gel forms that inhibits further flow of fresh acid into the wormhole. As the acid spends further (after the treatment) and the pH continues to rise, the reducing agent converts the ferric ions to ferrous ions and the gel reverts to a more fluid water-like state. Hydrazine salts and hydroxylamine salts are specified as the reducing agents.

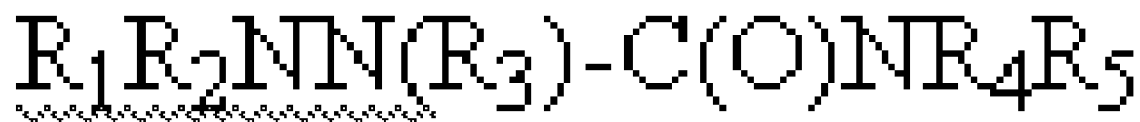
[0006] However, hydrazines and their salts are suspected carcinogens, and hydroxylamine salts are very reactive and can be used only at low temperatures. There are many reducing agents known that will reduce ferric ion to ferrous ion at a pH of about 2 or greater, but none has previously been tried in this system that did not suffer from a serious drawback. Furthermore, after these reducing agents have broken the crosslinked polymer gel, there is some residue left behind that can reduce the fluid conductivity of treated portions of the formation. There is a need for lower-toxicity reducing agents or reducing agents having suitable reactivity and compatibility with the other components of this system so that residue is reduced.

SUMMARY OF INVENTION

[0007] One embodiment of the Invention is an aqueous acid composition containing an aqueous acid; a polymeric gelling agent that crosslinks in the presence of ferric ions at a pH of about 2 or greater; a soluble ferric salt in an amount sufficient to crosslink the polymeric gelling agent at a pH of about 2 or greater, but which does not crosslink the polymeric gelling agent at a pH below about 2; and an effective amount of a source of a reducing agent, which is hydroxylamine or a hydrazine. The source of the hydrazine or hydrazines is either a carbohydrazide having the formula

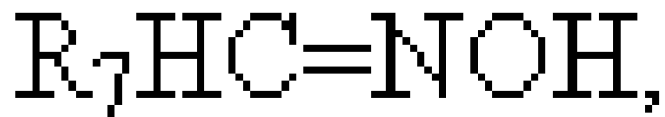


[0008] or a semicarbohydrazide having the formula

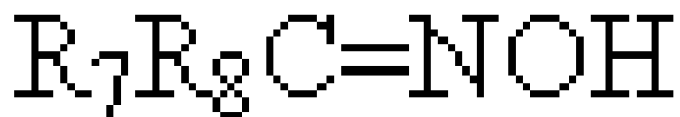


[0009] in which R_1 through R_6 may be the same or different and may be hydrogen or a branched, cyclic, or straight chained, or saturated or unsaturated hydrocarbon having from 1 to about 6 carbon atoms. The preferred source of a carbohydrazide is carbohydrazide itself, the compound

in which R_1 through R_6 are each hydrogen. The preferred source of a semicarbohydrazide is semicarbohydrazide itself, in which R_1 through R_5 are each hydrogen. The source of the hydroxylamine is either an aldoxime having the formula



[0010] or a ketoxime having the formula



[0011] in which R_7 and R_8 may be the same or different and may be a branched, cyclic, or straight chained, saturated or unsaturated hydrocarbon having from 1 to about 8 carbon atoms and may form a ring. The source of the hydroxylamine is preferably 2-butanone oxime, methyl isobutyl ketoxime, cyclohexanone oxime, acetaldoxime, butyraldoxime, propionaldoxime, heptaldoxime, 3-heptanone oxime, or acetophenone oxime. Most preferably, it is 2-butanone oxime.

[0012] Another embodiment of the Invention is a method of acidizing a subterranean formation penetrated by a well-

bore including the step of injecting one or more of the above fluids into the formation through the wellbore. Yet another embodiment is a method of acidizing in which the step of injecting into the formation through the wellbore is conducted at a pressure and flow rate sufficient to create a fracture in the formation (called acid fracturing or fracture acidizing).

DETAILED DESCRIPTION

[0013] European Patent No. 0 278 540 B1, and counterpart U. S. Patent Application No. 07/007409, filed January 27, 1987, now abandoned, and hereby incorporated by reference in its entirety, describes acids, polymers, iron crosslinking agents and reducing agents for LCA systems and SDA systems, and methods for their use, related to embodiments of the present Invention. It states that "The reducing agent to be used according to the present invention can generally be any such composition that effectively converts the Fe(III) to Fe(II) at spent acid condition, but is ineffective in live acid. Preferably, hydrazine and hydroxylamine salts are employed. As such, hydroxylamine hydrochloride is preferably used at lower relative temperatures while the less active hydrazine sulfate is employed at elevated temperatures." Only certain actual reducing agents are de-

scribed or claimed. Note that "live" acid is acid that is still strong enough to dissolve the formation and "spent" acid or fluid is acid that has reacted to the extent that it cannot still dissolve rock at a useful rate. (Another function of the reducing agent is to act as an "iron control agent" in the spent fluid. Ferric ion present at higher pH after the acid completely spends (coming into the system for example from connate water, injected water, or corrosion) can precipitate as ferric hydroxide (which occurs above a pH of about 3.2), or can re-crosslink the polymer.) According to that patent and application, sodium erythorbate was tried as a reducing agent, but was found to be too active in strong acid; a significant amount of the ferric ion was reduced below a pH of about 2 even at low temperatures. This had three disadvantages. First, more ferric iron was required so that enough would be left to crosslink the polymer. Second, more sodium erythorbate was required to ensure later reversal of the polymer crosslinking. Third, more sodium erythorbate was required so that there would be some remaining as an iron control agent. The preferred reducing agents were hydrazine sulfate or hydroxylamine hydrochloride. Note, however, that despite the statement in the specification of that patent and that

application that the reducing agent can be "any such composition that effectively converts the Fe(III) to Fe(II) at spent acid condition, but is ineffective in live acid" it is clear from the experimental results that not any such reducing agent can be used under any conditions. For example, some, such as hydroxylamine hydrochloride, are too active at high temperature.

[0014] GB Patent Application No. 2,163,790 described the use of reducing agents to prevent the crosslinking, in the presence of unwanted ferric ions, of polyacrylamide that had been added to HCl to thicken it to slow its reaction with carbonates in matrix acidizing. Experiments were performed at 65.6 °C and it was noted that in the absence of sodium erythorbate, polymer precipitates were found in solutions after HCl containing polyacrylamide was allowed to spend on marble chips, but no polymer precipitate or residue was observed in the spent gelled acid if sodium erythorbate was present. Therefore sodium erythorbate is an effective reducing agent for ferric ions in HCl and so would be too reactive for the purposes of the present Invention. Ascorbic acid was also said to be effective, but ascorbic acid would also not be suitable in the present Invention because it reduces ferric ions to ferrous ions at a

pH of less than 0.

[0015] U. S. Patent No. 4,693,954 describes a method and composition for stimulating subterranean formations containing iron deposits. When acidic, the composition includes a mixture of (i) at least one member selected from the group consisting of hydroxylamine hydrochloride, hydroxylamine hydrobromide, hydroxylamine sulfate, hydrazine monohydrochloride, hydrazine dihydrochloride, hydrazine sulfate, hydrazine monobromide, hydrazine dibromide, hydrazine monoiodide, hydrazine diiodide and hydroquinone together with (ii) at least one member selected from the group consisting of gluconodeltalactone, citric acid, salts of citric acid, ethylenediaminetetraacetic acid, salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, salts of nitrilotriacetic acid, hydroxyethylethylenediaminetriacetic acid, and salts of hydroxyethylethylenediamine-triacetic acid and (iii) a catalytic amount of a solubilized salt of a compound capable of providing cupric, cuprous, nickel, or zinc ions. The method consists of contacting the subterranean formation in an appropriate manner with the above-described composition present in an amount sufficient to sequester iron. In an acidic aqueous stimulating fluid the mixture is said

to substantially reduce any ferric ions in the stimulating fluid to ferrous ions and to scavenge at least a portion of the oxygen present in the aqueous fluid to substantially prevent the oxidation of the ferrous ions to ferric ions and thus substantially to prevent the precipitation of iron on the pore surfaces of the subterranean formation. No reason is given for the selection of the specific reducing agents listed, and no others are discussed.

[0016] Schlumberger has been using the following system commercially as an LCA system or an SDA system:

[0017] Polymer –
ethanaminium,N,N,N-trimethyl-methyl-oxo-chloride copolymer with propenamide (an anionic polyacrylamide) at temperatures below about 93 °C; or cationic polyacrylamide copolymer at temperatures above about 93 °C; each obtained as a concentrate in oil-external emulsion form.

[0018] Crosslinker – ferric chloride in water.

[0019] Reducing Agent – hydrazinium chloride in water

[0020] In a suitable LCA/SDA system, such as those of embodiments of the present Invention, the formulations have unique rheological properties. Crosslinking must not oc-

cur in live acid, so the reducing agent must not reduce ferric ion to ferrous ion in live acid. Initial spending of the live acid during leak-off and wormholing produces a rise in pH to a value of above about 2, which initiates crosslinking of the polymer (resulting in and evidenced by a rapid increase in viscosity). When the polymer is fully crosslinked, a viscosity of above about 1000 cp is normally obtained. This increase in viscosity creates the diversion from wormholes, from fissures, and within the matrix. The highly viscous acid will plug off the thief zone, forcing the following stage or stages of fresh live acid to be diverted. The lower viscosity fresh acid allows penetration into other wormholes and fractures, until the reaction of the fresh acid increases the pH value and causes crosslinking, thereby diverting the following acid stages to other portions of the reservoir. Acid in the well-bore and from subsequent treatment stages will keep the pH sufficiently low so that the viscosity will be maintained until the end of the job, at which time the acid is allowed to spend completely.

[0021] As the viscosified LCA/SDA acid system spends further, the pH continues to increase. The gel begins to break at a pH above about 3. The cross-linked gel structure of the

LCA/SDA system fluid collapses and the LCA/SDA system reverts back to a low viscosity fluid. Further pH increases to values above about 3.5 will reduce the viscosity to that of an uncrosslinked polymer thickened fluid at the well temperature. It has been observed that the retention of some viscosity after spending assists in maintaining the formation fines in suspension and facilitates an improved cleanup (if the reservoir is not too depleted). Since the gel begins to break at a pH above about 3 to 3.5, flowback represents no difficulty once fresh acid injection is stopped and the acid is allowed to spend completely.

[0022] For embodiments of the present Invention, we have found several classes of compounds, that are reducing agents or precursors of reducing agents, that are suitable for use in LCA/SDA systems to provide delayed ferric ion reduction. These compounds are less toxic to aquatic species than reducing agents used in the past. The precursors are converted into suitable reducing agents (hydrazines or hydroxylamine) during the LCA/SDA system treatment. They are much safer to handle for personnel and for the environment. Furthermore, these compounds can reduce the amount of residue remaining from the crosslinked polymer after treatments. Suitable compounds of the Invention

are sources of one or two hydrazines or sources of hydroxylamine; suitable compounds are carbohydrazides, semicarbohydrazides, ketoximes, and aldoximes. The hydrazines and hydroxylamine will form hydrochlorides in HCl.

[0023] Suitable carbohydrazides, $R_1 R_2 NN(R_3)-C(O)NR_4 NR_5 R_6$, and semicarbohydrazides, $R_1 R_2 NN(R_3)-C(O)NR_4 R_5$, are those in which R_1 through R_6 may be the same or different and may be hydrogen or a branched, cyclic, or straight chained, saturated or unsaturated hydrocarbon having from 1 to about 6 carbon atoms. These compounds hydrolyze to yield hydrazine and mono-, di-, and/or tri-substituted hydrazines. The preferred member of this class is carbohydrazide itself, the compound in which R_1 through R_6 are each hydrogen. The carbohydrazides and semicarbohydrazides are reducing agents themselves, but not to be limited by theory it is believed that under the conditions of use in embodiments of the Invention they hydrolyze rapidly to form hydrazine and mono-, di-, and/or tri-substituted hydrazines that are the predominant reducing agents in the system for ferric ions.

[0024] Suitable aldoximes, $R_7 HC=NOH$, and ketoximes, $R_7 R_8 C=NOH$, are those in which R_7 and R_8 may be the same

or different and may be a branched, cyclic, or straight chained, saturated or unsaturated hydrocarbon having from 1 to about 8 carbon atoms. In the ketoximes, R_7 and R_8 may form a ring. Aldoximes and ketoximes are condensation products, respectively, of aldehydes and ketones with hydroxylamine. In embodiments of the Invention, they hydrolyze to form hydroxylamine, which is the reducing agent for the ferric ions. Suitable aldoximes and ketoximes include, by non-limiting examples, methyl ethyl ketone oxime (often called methyl ethyl ketoxime, or 2-butanone oxime, the name that will be used here), methyl isobutyl ketoxime, cyclohexanone oxime, acetaldoxime, butyraldoxime, propionaldoxime, heptaldoxime, 3-heptanone oxime, and acetophenone oxime. The preferred member of this class is 2-butanone oxime.

[0025] The reducing agents or reducing agent precursors are preferably present in the final LCA/SDA aqueous fluid systems as solutions of from about 0.1 to about 0.3 weight percent active ingredient, preferably from about 0.1 to about 0.2 weight percent. The reducing agents or reducing agent precursors are preferably used as concentrates containing about 10% active ingredient in an aqueous solution to be added to the LCA/SDA aqueous fluid systems

before injection. Therefore the concentrates are typically added to the fluid systems at concentrations of from about 1 to about 3 weight percent, preferably from about 1 to about 32 weight percent. The actual concentration used, however, depends upon the actual concentration of ferric ion used and can be adjusted up or down accordingly.

[0026] In embodiments of the present invention, suitable polymers can be any polymer that is stable in an aqueous acid environment and that can be crosslinked in the presence of ferric ions at a pH of about 1 to 2 or greater. (Typically, crosslinking begins at a pH of about 1 but becomes strong at a pH of about 2 or greater. We will refer to this as crosslinking at a pH of about 2 or greater.) This will include any carboxyl-containing polymer, as generally known in the art. Preferably, and by way of example, but not limited thereto, such polymers include acrylamide and acrylamide copolymers (particularly partially hydrolyzed acrylamide polymers and copolymers), xanthan gums, carboxymethyl cellulose, carboxyhydroxymethyl cellulose, carboxymethylhydroxypropyl guar and related gums or polymers having pendant carboxyl groups to which the Fe(III) can crosslink. Particularly preferred polymers ac-

cording to the present Invention are ethanaminium,N,N,N-trimethyl-methyl-oxo-chloride copolymer with propenamide (an anionic polyacrylamide) at temperatures below about 93 °C; and cationic polyacrylamide at temperatures above about 93 °C; each obtained as a concentrate in oil-external emulsion form. Another preferred polymer is a cationic acrylamide emulsion involving a copolymer of 2.5 mole % acrylamide and 7.5 mole % dimethylaminoethylmethacrylate quaternary acid salt. Typically, such polymers are obtained as concentrated oil-in-water emulsions containing from about 20 to about 50 weight % polymer; a 35 weight % emulsion would typically be used at about 20 to 30 L/1000L concentration in the final LCA/SDA system, depending upon the temperature and the desired viscosity.

[0027] In embodiments of the present Invention, suitable acidscan be any acid generally used in fracture acidizing or matrix acidizing, including by way of example, but again not limited thereto, HCl, HBr, HF and mixtures thereof, other mineral acids, acetic acid, formic acid, other organic acids as long as they are not strong reducing agents or strong chelating agents, mixtures thereof, and mixtures thereof with mineral acids. For an LCA system, preferably,

an HCl solution of from about 10% up to about 28% or even greater is to be employed. SDA fluid system embodiments may often contain less acid. If the fluid is to be used as a diverter only, and crosslinking is desired to occur as close to the wellbore as possible, then the preferred acid concentration is from about 3% to about 7.5%, and the preferred acid is HCl.

[0028] In embodiments of the present Invention, suitable iron sources can generally be any source of ferric ion. Soluble ferric salts such as FeCl_3 , $\text{Fe}(\text{NO}_3)_3$, FeBr_3 , or the like are preferred. It has been found that as little as 25 ppm Fe(III) has a pronounced effect on wormhole growth. The upper limit of Fe(III) concentration can in principle approach saturation or the solubility limits of the system, provided that sufficient reducing agent is present to reverse the crosslinking of the polymer after spending of the acid. Preferably, the limits of Fe(III) would be from about 100 to about 1000 ppm.

[0029] In embodiments of the present Invention, many other components may be included provided that they are compatible with all components of the LCA/SDA system and do not unduly interfere with its performance. Typical additives that may be included are surfactants, silicate con-

trol additives, emulsion and sludge preventers, and non-emulsifying agents. Corrosion inhibitors should always be used to protect oilfield equipment and tubulars, but not all corrosion inhibitors are compatible with LCA/SDA system embodiments. Commercial corrosion inhibitor packages are typically mixtures of many compounds, some of which may irreversibly gel the polymers or may be reducing or oxidizing agents. Commercial corrosion inhibitor packages should therefore always be tested before use for compatibility with the LCA/SDA fluid system being used. Furthermore, the following additives are not compatible with LCA/SDA system embodiments of the Invention and should not be used: tetrasodium EDTA chelating agent, citric acid chelating agent, trisodium nitrilotriacetic acid chelating agent, and ammonium thioglycolate iron reducing agent, which is sometimes used in acid systems for iron control but is too active a reducing agent to be used in LCA/SDA applications. Other additives may also be incompatible, and all additives should be tested for compatibility with the LCA/SDA fluid system being used. If H_2S is present, either naturally or from dissolution of iron sulfide scale by the acid, then additional suitable reducing agent or reducing agent precursor of the Invention should

be added to make up for the reducing agent that will be consumed by reaction with the H_2S .

[0030] LCA/SDA system embodiments of the Invention may be batch-mixed or continuous-mixed. Mixing tanks should be clean and free of rust. Mixing is preferably done with a centrifugal mixer rather than air lancing. Mixing in the following order will prevent lumping (fish-eyes) with mixing equipment commonly used in the field. Add mix-water to the tank, then add corrosion inhibitors and other additives, then add the concentrated acid. While mixing, then add the reducing agent or reducing agent precursor slowly to minimize heat generation; then add the iron source, and finally add the polymer. For continuous mixing, any or all of the components except the polymer may be pre-mixed in the acid and the polymer may then be continuously mixed during the treatment.

[0031] When used as an SDA system, fluid embodiments of the Invention are most typically pumped in several stages alternately with regular acid stages. These SDA fluid systems contain no solids or particulates, which could bridge when pumping through coiled tubing. These SDA fluid systems can be used in either cased or openhole completions, since they actually divert in the formation rather

than onit (*in situ* diversion). These SDA fluid system properties are similar to a gelled acid system. Treatments are staged by pumping "slugs" of the SDA fluid system. Treatments can be bull-headed, but the best results are obtained from using the SDA system down coiled tubing. The SDA system diversion has the greatest potential in horizontal wells, and in treating zones with widely varying permeability streaks. When used with coiled tubing for placement, the SDA fluid system embodiments provide an optimum technique for diverting in carbonate reservoirs. As there are no damaging solid particles in the SDA fluid system, the broken SDA fluid is readily flowed back from the well along with the remains of the spent acid from the treatment. When used as an LCA system, fluid embodiments of the Invention may be used, among options, alone in a treatment (as the fracturing fluid) or may be used with a nonreactive pad. The reducing agents or reducing agent precursors of the Invention may also be used as iron control agents.

[0032] Although the methods have been described here for, and are most typically used for, hydrocarbon production, they may also be used in storage wells and injection wells, and for production of other fluids, such as water or brine.

[0033] One skilled in the art would appreciate that modifications may be made without departing from the scope of the Invention. While the Invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the Invention as disclosed herein. Accordingly, the scope of the Invention should be limited only by the attached claims.

[0034] *Examples* Four reducing agents or reducing agent precursors were evaluated, as shown in Table 1 below:

Compound	Commercial Name	CAS No.	Activity (% Aqueous) As Used
2-Butanone oxime	MEKOR 6701 / Ashland	96-29-7	10%
Carbohydrazide	ELIMINOX / Ondo Nalco	497-19-7	12%
Diethylhydroxyl amine	-	3710-84-7	85%
Hydrazinium hydrochloride	-	2644-70-4	33%

Table 1

[0035] The 2-butanone oxime was obtained from Ashland Specialty Chemical Company, Dublin, OH, U. S. A. under the trade name MEKOR 6701, and the carbohydrazide was obtained from Ondo Nalco Company, Houston, TX U. S. A., under the trade name ELIMINOX.

[0036] *Ecotoxicity:* Results of bioaccumulation, biodegradation and

toxicity testing for three compounds are shown in Table 2. The bioaccumulation testing was done according to Organization of Economic Co-operation and Development, Paris, (OECD) Method 117. The biodegradation tests were done according to OECD 306. The toxicity tests were done according to the protocol required for application in the North Sea as recommended by OSPAR (the Oslo Paris Commission) for completion of HOCNF (Harmonized Off-shore Chemical Notification Format) requirements. The methods are those in effect as of August, 2003, and the MSDS data and public health, safety and environment data given below are as of August, 2003.

Composition		Bioaccumulation	Biodegradability	Toxicity Results		
Component	%	Log P _{ow}	BOD 28 day	<i>Skeletonema Costatum</i> EC50 72 hr	<i>Acartia tonsa</i> LC 50 48 hr	<i>Scophthalmus maximus</i> <i>juvenile</i> EC 50 96 hr
2-butanoneoxime Water	10 90	1.38	6%	470 mg/L	6934 mg/L	> 3000 mg/L
Carbohydrazide Water	12 88	nd	nd	56.7 mg/L	nd	nd
Hydrazinium-HCl Water HCl	33 66 1	< 0	84%	0.38 mg/L EC50 24hr	0.37 mg/L	<i>Abra alba</i> 96 mg/L

nd = not determined

Table 2

[0037] It can be seen that the examples of suitable compounds of embodiments of the Invention, 2-butanone oxime and carbohydrazide, show less probable bioaccumulation and are about 1 to 4 orders of magnitude less toxic to aquatic

organisms than the hydrazinium hydrochloride.

[0038] Diethylhydroxylamine is rated in MSDS"s as harmful and an irritant. There is also evidence of mutagenicity and reproductive function effects. The product may also cause allergic reactions. MSDS"s state that there is a possible risk of irreversible effect and that it is a possible sensitizer. Biodegradation testing according to OECD 306B (done in seawater according to the test method of the Organization for Economic Co-operation and Development, Paris, France) indicates less than 60% biodegradation. The literature value for bioaccumulation ($\text{Log } P_{ow}$) is 0.43 by HPLC Method OECD 117.

[0039] Carbohydrazide is described in MSDS"s as harmful and an irritant, because it hydrolyzes to hydrazine.

[0040] 2-Butanoneoxime is classified as a severe eye and skin irritant, as harmful by ingestion and as a skin sensitizer. However, in addition to the excellent toxicity results shown in Table 2, in further OSPAR tests, 2-butanoneoxime had NOEC (No Observable Effect Concentration) values of 8.9 mg/L for *Acartia tonsa* (48 hours), 1000 mg/L for *Scophthalmus maximus juvenile* (96 hours), and 99.7 mg/L for *Skeletonema Costatum* (72 hours), and the 15 day BOD was 6.5%.Hydrazinium hydrochloride is toxic by all

routes, and is a possible carcinogen (Category 2) and mutagen. Hydrazine is a skin sensitizer and is toxic to aquatic species.

[0041] Hydrazinium hydrochloride is toxic by all routes, and is a possible carcinogen (Category 2) and mutagen. Hydrazine is a skin sensitizer and is toxic to aquatic species. Iron Reduction Performance: All solutions were prepared as indicated using about 0.5% by volume of a concentrate having about 40 weight percent FeCl_3 , and analyses were done with a HACH 2000 colorimeter, obtained from Hach Company, Loveland, CO. Standard analyses were as described in the "Water Analyses Handbook," Hach Company. Total iron was obtained by the FerroZine procedure by formation of a purple complex observable at 562nm. The ferrous iron content was determined by the phenanthroline complex procedure determined at 510nm. An orange complex is formed which is proportional to the iron content. For each analysis, samples of the test solution were taken and diluted 1:100 with water and the appropriate, premeasured reagent pillows were added to the solution. Measurements were determined colorimetrically employing standards for the analyses. For ferrous content, analyses were made quickly to prevent oxidation due to air. Total iron required 5 minutes reaction time. If ferric con-

tent was needed, the content was obtained by difference.

Test 1: DI water + 0.50% FeCl ₃ (pH 2.03)								
Reagent	Carbohydrazide (12%)			2-Butanone oxime (10%)			Diethylhydroxyl amine (12%)	
Concentration	Iron Content			Iron Content			Iron Content	
		mg/L	% reduced		mg/L	% reduced		mg/L % reduced
Total Iron	Fe⁺³	1430		Fe⁺³	770		Fe⁺³	1020
0.25 %	Fe⁺²	230	16.1 %	Fe⁺²	250	32.5 %	Fe⁺²	420 41.2 %
0.50 %	Fe⁺²	390	27.3 %	Fe⁺²	400	51.9 %	Fe⁺²	670 65.7 %
0.75 %	Fe⁺²	500	35.0 %	Fe⁺²	520	67.5 %	Fe⁺²	670 65.7 %
1.00 %	Fe⁺²	550	38.5 %	Fe⁺²	560	72.7 %	Fe⁺²	750 73.5 %
1.25 %	Fe⁺²	670	46.9 %	Fe⁺²	640	83.1 %	Fe⁺²	770 75.5 %
1.50 %				Fe⁺²	700	90.9 %	Fe⁺²	860 84.3 %
2.00 %							Fe⁺	2 910 89.2 %

Test 2: 15% HCl + 0.50% of a 40% FeCl ₃ Aqueous Solution								
Reagent	Carbohydrazide (12%)			2-Butanone oxime (10%)			Diethylhydroxyl amine (12%)	
Concentration	Iron Content			Iron Content			Iron Content	
		mg/L	% reduced		mg/L	% reduced		mg/L % reduced
Total Iron	Fe⁺³	1310		Fe⁺³	930		Fe⁺³	1020
0.25 %	Fe⁺²	10	0.8 %	Fe⁺²	20	2.2 %		
0.50 %	Fe⁺²	10	0.8 %	Fe⁺²	30	3.2 %	Fe⁺²	350 34.3 %
0.75 %	Fe⁺²	10	0.8 %	Fe⁺²	70	7.5 %		
1.00 %	Fe⁺²	160	12.2 %	Fe⁺²	90	9.7 %	Fe⁺²	490 48.0 %
1.25 %	Fe⁺²	390	29.8 %	Fe⁺²	100	10.8 %		
1.50 %	Fe⁺²			Fe⁺²	130	14.0 %	Fe⁺²	540 52.9 %
2.00 %							Fe⁺²	850 83.3 %

Test 3: 50% water/CaCl ₂ + 10% 15% HCl + 0.50% FeCl ₃								
Reagent	Carbohydrazide (12%)			2-Butanone oxime (10%)			Diethylhydroxylamine (12%)	
Concentration	Iron Content			Iron Content			Iron Content	
		mg/L	% reduced		mg/L	% reduced		mg/L
Total Iron	Fe ⁺³	1230		Fe ⁺³	460		Fe ⁺³	1250
0.25 %	Fe ⁺²	140	11 %	Fe ⁺²				
0.50 %	Fe ⁺²	160	13 %	Fe ⁺²	80	17 %	Fe ⁺²	310
0.75 %	Fe ⁺²	170	14 %	Fe ⁺²				
1.00 %	Fe ⁺²	190	15 %	Fe ⁺²	100	22 %	Fe ⁺²	520
1.25 %	Fe ⁺²	190	15 %	Fe ⁺²				
1.50 %				Fe ⁺²	170	37 %	Fe ⁺²	590
2.00 %							Fe ⁺²	760

Table 3

[0042] Tests were done to determine the effect of pH and concentration of reducing agent or reducing agent precursor on the iron reduction process. The procedures for the iron analyses were described above. The concentration of reducing agent was varied to determine the concentration required to achieve complete reduction at a pH of 2 (Test 1). Deionized water was used and 0.5% FeCl₃ was added. The pH of the system was adjusted to pH 2 prior to addition of reducing agent. Table 3 shows that slower reduction occurred with the carbohydrazide. The fastest reduction occurred with diethylhydroxylamine. Similar results were observed with full strength acid (Test 2) and partially spent HCl (Test 3). Diethylhydroxylamine was too active in the reduction of iron at the lower pH. Carbohydrazide and 2-butanone oxime were approximately equivalent.

[0043] The selected iron reducing agent should not reduce the ferric iron in acid solutions. To further demonstrate that the iron reduction is minor until 99% of the acid spends, iron reduction was observed as a function of HCl spending, as shown in Table 4. Five tests were done, at 0% spent, 90% spent, 95% spent, 99% spent and 99.5%. For each of these tests 2.0% of an approximately 10 to 12% aqueous solution or reducing agent or reducing agent precursor was evaluated. This represents approximately twice the concentration to adequately reduce the quantity of Fe^{+3} present. Again, the diethylhydroxylamine reduced the ferric iron too easily. Very little reduction was observed for the carbonylhydrazide. Minimal reduction occurred with the 2-butanone oxime with the live acid; however, more than 80% reduction was observed with 99.5% spent acid. Based on these series of tests, the 2-butanoneoxime performs most satisfactorily, carbonylhydrazide is less preferred and diethylhydroxylamine is not suitable.

Reagent:		Carbohydrazide (12%)		2-Butanone oxime (10%)		Diethylhydroxylamine (12%)	
Concentration		Iron Content		Iron Content		Iron Content	
		mg/L	% Reduced	mg/L	% Reduced	mg/L	% Reduced
Test 1: 15% HCl + 0.50% FeCl ₃							
Total Iron	Fe ⁺³	1140		1140		1140	
2.00 %	Fe ⁺²	20	1.8 %	100	8.8 %	620	54.4 %
Test 2: 90% Spent 15% HCl + 0.50% FeCl ₃							
Total Iron	Fe ⁺³	1130		1130		1130	
2.00 %	Fe ⁺²	90	8.0 %	300	26.5 %	750	66.4 %
Test 3: 95% Spent 15% HCl + 0.50% FeCl ₃							
Total Iron	Fe ⁺³	1250		1250		1250	
2.00 %	Fe ⁺²	20	1.6 %	140	11.2 %	930	74.4 %
Test 4: 99% Spent 15% HCl + 0.50% FeCl ₃							
Total Iron	Fe ⁺³	800		800		800	
2.00 %	Fe ⁺²	160	20.0 %	420	52.5 %	710	88.8 %
Test 5: 99.5% Spent 15% HCl + 0.50% FeCl ₃							
Total Iron	Fe ⁺³	730		730		730	
2.00 %	Fe ⁺²	90	12.3 %	610	83.6 %	650	89.0 %

Table 4

[0044] *Rheology and Break Time:* Fluids were made up containing 15% HCl, 2% of a cationic polyacrylamide copolymer, 1% of a standard corrosion inhibitor, 0.25% FeCl₃ and 1 and 2% of carbohydrazide, diethylhydroxylamine, or 2-butanione oxime. The viscosities as measured with a Fann 35 Rheometer of all the gelled acids were about the same initially and were about like one another after 1 hour at 65.5 °C at shear rates from about 5 to about 1000 sec⁻¹. The crosslink time was determined in the presence of carbohydrazide, 2-butanoneoxime, and hydrazinium hy-

drochloride. A solution of 4.2% HCl containing 2% ethanaminium,N,N,N-trimethyl-methyl-oxo-chloride copolymer with propenamide (an anionic polyacrylamide) and 0.25% FeCl_2 and the desired reducing agent or reducing agent precursor was added to a Warring blender cup and mixed at minimal speed to avoid mixing of air into the system. The acid was quickly neutralized by addition of a solution of sodium carbonate. The required quantity was calculated to be certain that only sufficient quantity was used to spend the acid. A defoamer was added to minimize the foaming that occurs during the rapid neutralization and evolution of carbon dioxide. The crosslinking occurred immediately with the ferric iron on neutralization of the acid in each case. The reducing agent controls the breaking of the crosslink. The time required for the break was determined from the time the sodium carbonate was added, closing the vortex in the mixed fluid in the blender, to the time that the vortex reformed, signifying the breaking or reduction of the iron crosslinking of the acid. The results are shown in Table 5; the carbohydrazide and 2-butanoneoxime showed a slightly longer break time than observed with hydrazinium hydrochloride.

Reducing Agent		Crosslink Break Time (min:sec)	pH	
Percent	Reagent		Initial	Final
1.0%	Hydrazinium hydrochloride	2:35	~2	~7
2.0%	"	2:10	~2	~7
1.0%	2-butanone-oxime	3:30	~2-3	~7
2.0%	"	1:20	~2-3	~7
1.0%	Carbohydrazide	3:50	~2-3	~7
2.0%	"	0:50	~2-3	~7

Table 5

[0045] *Acid Spending Tests:* Spending tests of the gelled acid were done with Indiana Limestone chips. Tests were done using gelled 15% HCl containing 3% cationic polyacrylamide copolymer, 0.5% of an approximately 40% aqueous solution of FeCl_3 and either 1% of 33% hydrazinium hydrochloride in water, 6% of 12 % carbohydrazide in water, or 10% of 2-butanoneoxime in water. The gels were placed in a cell containing carbonate chips and allowed to spend for 6 hours under ambient pressure at 6.89 mPa pressure at 65.5 °C and 121 °C respectively. An excess of carbonate chips was used to facilitate the spending of the acid. Somewhat varied spending of the limestone was noted, but all were effective. Carbohydrazide was most effective at 65.5 °C while 2-butanone oxime was most effective at 121 °C. The results are summarized in Table 6.

Note that when the tests at 6.89 mPa were ended, the gel appeared still to be reacting.

Test Temp (°C)	Test Press (mPa)	Reducing Agent	Amount Limestone Dissolved (%)
65.5	Ambient	1% Hydrazinium hydrochloride	24.8
65.5	Ambient	1% Carbohydrazide (12%)	33.4
65.5	Ambient	1% 2-Butanone Oxime	24.2
65.5	Ambient	2% Carbohydrazide (12%)	24.6
65.5	Ambient	2% 2-Butanone Oxime	29.2
65.5	6.89	2% 2-Butanone Oxime	25.4
121	6.89	2% 2-Butanone Oxime	44.6
121	6.89	1% Hydrazinium hydrochloride	29.5
121	6.89	2% Carbohydrazide (12%)	31.1

Table 6

[0046] To evaluate the spending of the gelled acid further, experiments were done at 121 °C and the visual appearance of the gel and the quantity of residue were determined. The recovery of the gel from the carbonate chips was done by filtration of the gel through a wire screen. When hydrazinium hydrochloride was used as the reducing agent, the experiments clearly showed the presence of crosslinked gel still present. When carbohydrazide was used, the experiments showed less crosslinked gel but there was still considerable gel residue. For the gel prepared with 2-butanone oxime, the carbonate chips were cleaner and there was less residue and greater dissolution

of the carbonate chips than observed for the hydrazinium hydrochloride or carbohydrazide in similar tests. The results of these tests showed that a cleaner break was achieved with the 2-butanoneoxime than for the hydrazinium hydrochloride at 121 °C. The gel was broken when 2-butanoneoxime was used; the fluid showed some viscosity, but no crosslinking. When hydrazinium hydrochloride was used, the fluid still showed viscosity and a slightly crosslinked character. The gelled acid system with the new reducing agents or reducing agent precursors offered improved clean up of the spent acid with less residue that could impede fluid flow during flow back of the spent gelled acid.

[0047] Acid spending tests were designed and implemented to analyze for residue for spending tests completed at 121 °C. These tests were done with amounts chosen such that not all the limestone could be dissolved. A solution of 15% HCl acid gelled with 2% cationic polyacrylamide copolymer and 0.25% FeCl_3 was prepared with analytical grade HCl and deionized water. Reducing agents and reducing agent precursors were evaluated and compared with hydrazinium hydrochloride. Indiana Limestone was crushed and approximately 25 grams of the limestone chips were

placed in a jar that would fit a small autoclave. The gelled acid (2.25-ml of gelled acid solution per gram of chips) was added to the limestone chips, stirred to mix well, placed in the autoclave, pressurized to 6.89 mPa, heated to 121 °C and maintained for six hours. At the conclusion of the test, the autoclave was cooled and depressurized. The jar and contents were removed for examination and analysis.

[0048] The spent gelled acid was poured through a strainer to observe the fluid and to determine whether the gel was broken. The chips were also rinsed with deionized water to remove gel and residue from the chips, which were examined and then dried and the final weight determined. All residues were rinsed from the jar and chips, combined, and filtered through a pre-weighed Whatman 541 filter paper. The filter paper was dried to a stable weight to obtain the residue weight.

[0049] The data are recorded in Table 7. These results again show that a greater percent of the limestone is reacted with the limestone chips with the 2-butanoneoxime as reducing agent precursor than observed with the hydrazinium hydrochloride reducing agent. The tests also indicated less residue was left after use of

2-butanoneoxime than after use of hydrazinium hydrochloride. Not shown is that the percent of iron observed in the residues was about the same.

Reagent	Residue Remaining (g)	Rock Consumed (%)	Acid Spent (%)
Hydrazinium Hydrochloride	0.278	32.6	58.5
2-Butanone Oxime	0.165	42.2	76.3

Table 7

[0050] *Diversion:* Tests were completed with one-inch diameter and 4inch length cores of Indiana Limestone. The initial permeability of each was determined with 3% NaCl brine in both the production and treatment directions prior to treatment with the gelled acid fluid. Then the gelled fluid was pumped at a constant pressure of about 0.345 mPa in the treatment direction. The time for acid break-through was also recorded. All tests were completed at 65.5 °C and constant pressure. Three cores were used to test for diversion in each case; two cores were about 18 to about 24 md and 1 core was about 45 to about 60 md. The initial and final permeabilities were determined. After the tests, all cores were CT scanned, cross sectional view, to visualize the wormholing. The fluid evaluated was a typical SDA fluid system containing 5% HCl, 3% cationic polyacrylamide copolymer and 0.25% crosslinking agent FeCl_3 . Re-

ducing agent hydrazinium hydrochloride (1% of 40 % aqueous solution) and hydroxylamine source 2-butanoneoxime (2% of 10% aqueous solution) were tested. The results are shown in Table 8.

Reagent	Core	Initial Permeability	Final Permeability
Hydrazinium Hydrochloride	1	17.9 md	14.1 md
	2	60.4	>5000
	3	19.0	6.8
2-Butanone Oxime	1	24.1	34.1
	2	46.0	>5000
	3	21.2	49.6

Table 8

[0051] These diversion studies resulted in wormhole formation and were ended after the wormhole broke through the highest permeability core in each test. The gelled acid containing the hydrazinium hydrochloride exhibited decreases in permeability in the lower permeability cores. However increases in permeability of the lower permeability cores was observed with the gelled acid containing the 2-butanoneoxime. The acid containing hydrazinium hydrochloride diverted only slightly to core 1 (with a wormhole extending about 30% into the core) and appeared not

to have formed a wormhole at all in core 3. This is consistent with the final results where more damage was observed in core 3 than 1. The gelled acid that contained the 2-butanone oxime initially diverted the gelled acid to both cores lower permeability cores. This resulted in deeper penetration of the acid into core 3 (about 80% of the length) than into core 1 (at least 30%). This explains the higher retained permeability in core 3.

[0052] *Use of an LCA/SDA System:* To 100 ml of a 3% HCl solution in water being stirred on low speed in a Waring blender was added 0.5 ml of 10 weight % 2-butanone oxime in water. To this mixture was added 2 ml of 35 weight % cationic polyacrylamide copolymer oil-external emulsion in water with stirring and the fluid was mixed until the polymer was fully hydrated and the viscosity was about 25 cP. To this fluid was added 0.25 ml of 40 weight % ferric chloride in water and the mixture was stirred until the ferric chloride was fully dispersed. The viscosity remained low. To this mixture, with continued stirring, was added 20 ml of a slurry previously prepared from 50 g calcium hydroxide and 200 ml fresh water. As the acid reacted with the calcium hydroxide, the pH increased to about 2, the polymer crosslinked, and the viscosity increased to about 1000 cP.

Additional calcium hydroxide slurry was added with continued stirring, and as the pH rose to about 3.5, the viscosity was reduced back to the viscosity of the mixture before the ferric chloride had been added. 2-Butanone oxime is a suitable reducing agent precursor embodiment of the Invention.